LA-1325

Subject Category: PHYSICS

UNITED STATES ATOMIC ENERGY COMMISSION

THE CRYSTAL STRUCTURE OF GAMMA PLUTONIUM

By
W. H. Zachariasen

September 1951

Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Technical Information Extension, Oak Ridge, Tennessee

Date Declassified: March 15, 1956.

This report has been reproduced directly from the best available copy.

Issuance of this document does not constitute authority for declassification of classified material of the same or similar content and title by the same authors.

Printed in USA. Price 15 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AEC, Oak Ridge, Tenn.

LOS ALAMOS SCIENTIFIC LABORATORY
of the
UNIVERSITY OF CALIFORNIA

Report Written:
September 1951

LA-1325

THE CRYSTAL STRUCTURE OF GAMMA PLUTONIUM

by
W. H. Zachariasen

Work performed under Contract No. W-7405-Eng-36

ABSTRACT

Gamma plutonium is found to be orthorhombic with eight atoms in a unit cell of dimensions (at 226^{O}C) a_1 = 3.1518 kX, a_2 = 5.7568 kX, a_3 = 10.142 kX. The calculated density is 17.13. The space group is Fddd and the positions of the eight atoms are: (0 0 0) (0 1/2 1/2) (1/2 0 1/2) (1/2 1/2 0) (1/4 1/4 1/4) (1/4 3/4 3/4) (3/4 1/4 3/4) (3/4 3/4 1/4).

Each plutonium atom is bonded to ten others at an average distance of 3.152 kX, four being at 3.020 kX, two at 3.152 kX and four at 3.285 kX.

The coefficients of thermal expansion are found to be $\alpha_{100} = -22.5 \times 10^{-6}$, $\alpha_{010} = +47 \times 10^{-6}$, $\alpha_{001} = +94 \times 10^{-6}$

THE CRYSTAL STRUCTURE OF GAMMA PLUTONIUM

By

W. H. Zachariasen

The crystal structure is known for only two of the five allotropic forms of plutonium metal. The delta modification is cubic face-centered[1] with a = 4.63 Å [2] (at 350°C), and the epsilon form is cubic body-centered with a = 3.63 Å [3] (at 510°C).

Satisfactory X-ray diffraction patterns of the alpha, beta and gamma forms of plutonium have been available for several years. However, the indexing of these powder patterns has proved to be a very difficult task. The indexing of the pattern of gamma plutonium given in this report succeeded only after a great many hours of intensive work. The patterns of alpha and beta plutonium have not yet been interpreted.

Table 1 gives the observed intensities and sine squares as obtained from a powder diffraction pattern of gamma plutonium taken with CuKα-radiation at 226°C. The $\alpha_1\alpha_2$-doublet is separated for $\sin^2\theta > 0.400$, and the measurements refer to the stronger component.

The observed sine squares fit the quadratic form

$$\sin^2\theta = 0.05948\ H_1^2 + 0.01728\ H_2^2 + 0.005745\ H_3^2.$$

The corresponding orthorhombic unit cell has dimensions $a_1 = 3.1518 \pm 0.0004$kX, $a_2 = 5.7568 \pm 0.0008$kX, $a_3 = 10.142 \pm 0.002$ kX. Since the experimentally determined density is 17.0, the unit cell contains eight atoms. The calculated density is $\rho = 17.13$.

The translation lattice is face-centered as shown by the fact that reflections are present only from planes for which $H_1\ H_2\ H_3$ are either all even or all odd. It is further seen from Table 1 that reflections are missing from planes with $H_1\ H_2\ H_3$ all even unless $\Sigma H_j = 4n$.

According to these systematic absences the plutonium atoms are arranged on two interpenetrating face-centered lattices displaced relative to each other by one-fourth of the body diagonal. The positions of the eight atoms in the unit cell are thus: (0 0 0) (0 1/2 1/2)

TABLE 1. X-RAY DIFFRACTION DATA FOR GAMMA PLUTONIUM (226°C).

Int. obs.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	$H_1H_2H_3$	Int. calc.
s	0.0836	0.0830	111	142
w	925	919	004	61
m+	949	943	022	115
m	1297	1290	113	80
m-	2218	2209	115	36
w+	2265	2257	131	36
w+	2616	2609	202	28
w+	2723	2717	133	26
w+	2788	2781	026	25
vw	2860	2853	040	12
w+	3100	3092	220	21
w	3590	3588	117	17
w	3637	3636	135	16
vw	3687	3677	008	8
w+	3772	3772	044	15
m	4012	4011	224	30
w	4448	4447	206	12
w-	5017	5015	137	9
w-	5111	5110	151	9
vw	5427	5426	119	9
m*	5461	5462	242	18
vw	5574	5570	153	9
w*	5597	5588	311	9
vw+	6046	6048	313	8
vw+	6458	6458	0.2.10	8

*Coincidence with α_2 - line.

Int. obs.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	$H_1H_2H_3$	Int. calc.
w-*	6490	6489	155	8
w*	6526	6530	048	8
w-	6648	6649	062	8
w+	6766	6769	228	15
vw+	6853	6853	139	8
vw+	6970	6967	315	8
w*	7011	7015	331	8
m-	7300	7300	246	15
w-	7473	7475	333	8
vw	7724	7724	1.1.11	8
w-	7870	7868	157	8
w-	8125	8124	2.0.10	8
vw-	8273	8273	0.0.12	4
w-	8345	8346	317	9
w+*	8392	8394	335	9
w	8486	8487	066	9
w	8800	8798	260	10
w-	9150	9151	1.3.11	12
w	9388	9390	171	13
vw	9517	9517	400	8
ms	9717	9706	159	19
		9717	264	38
m*	9768	9773	337	21
w+	9849	9850	173	27
w+	9867	9868	351	29

(1/2 0 1/2) (1/2 1/2 0) (1/4 1/4 1/4) (3/4 3/4 1/4) (3/4 1/4 3/4) (1/4 3/4 3/4). This atomic configuration corresponds to the space group symmetry Fddd (D_{2h}^{24}) with the eight plutonium atoms structurally equivalent. A perspective drawing of one unit cell is shown in Figure 1.

The last column of Table 1 gives the intensities calculated from the formula

$$I \alpha \mid F \mid^2 \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}$$

The absorption and temperature factors have not been taken into account. Observed and calculated intensities should accordingly be compared only for neighboring reflections.

The crystal structure of gamma plutonium is unlike that of any other metal. Each plutonium atom is bonded to ten others at approximately the same distance, as illustrated in Figure 2. The individual interatomic distances are (at 226°C): Pu - 4Pu = 3.020 kX, Pu - 2Pu = 3.152 kX, Pu - 4Pu = 3.285 kX. The average distance of Pu - 10Pu = 3.16Å compares to Pu - 12Pu = 3.27Å in delta plutonium and Pu - 8Pu = 3.15Å in epsilon plutonium.

When allowance is made for the effect of coordination number one finds a metallic radius of 1.60Å for plutonium in the gamma form as compared to the radius 1.63Å in delta plutonium. The difference in radius for the two forms is possibly due to the fact that the transition from the delta to the gamma form is accompanied by the promotion of a fraction of an electron from the 5f to the 6d level. From the value of 1.60Å for the radius of plutonium in the gamma form, one would estimate that there are about three electrons in the 5f shell.

Normal to the a_3-axis there are pseudo-hexagonal layers, the a_3-period corresponding to four times the layer separation. The bond lengths within a layer are 3.152 kX and 3.285 kX. The bond length between layers is 3.020 kX.

Table 2 shows the variation of the unit cell dimensions with temperature in the range 161° - 265°C, and Table 3 gives the deduced values of the three principal coefficients of thermal expansion.

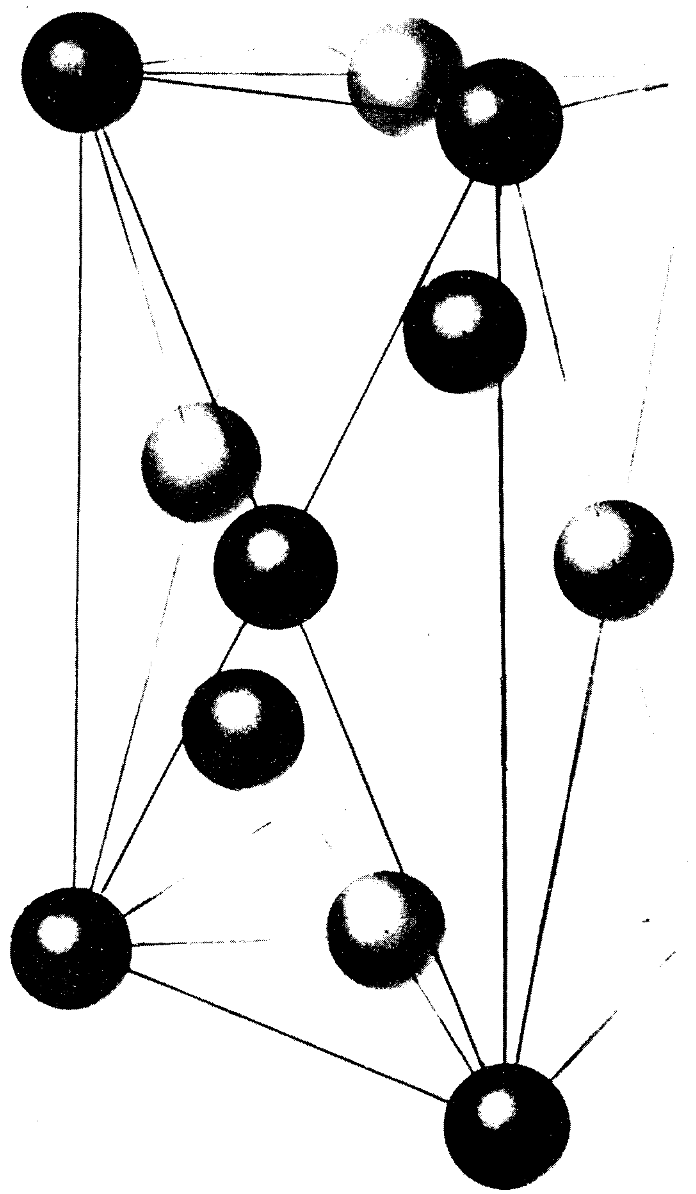

Fig. 1. The Unit Cell of Gamma Plutonium.

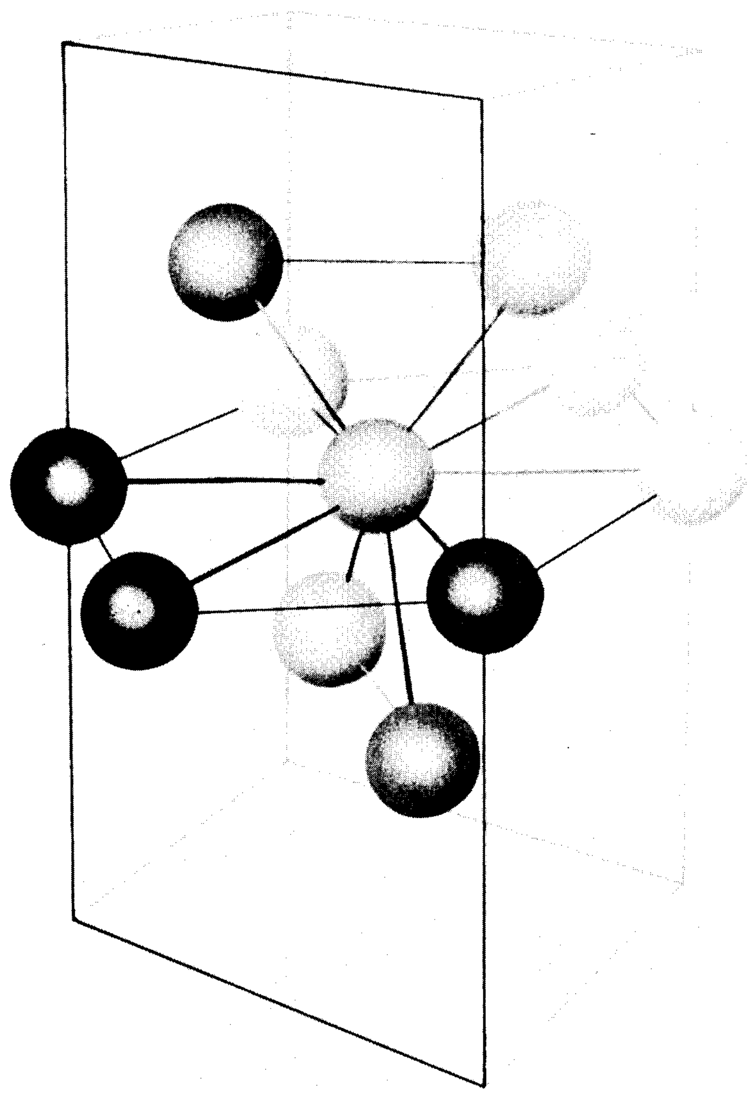

Fig. 2. A portion of the unit cell illustrating the tenfold coordination. Relative to Figure 1, the origin of the unit cell has been displaced by (0 0 1/2).

TABLE 2. UNIT CELL DIMENSIONS (IN kX) AND CALCULATED DENSITY AT VARIOUS TEMPERATURES

	161°	200°	226°	265°	Accuracy
a_1	3.1568	3.1527	3.1518	3.1490	$\pm$0.0004 kX
a_2	5.7400	5.7475	5.7568	5.7670	$\pm$0.0008
a_3	10.083	10.111	10.142	10.180	$\pm$0.002
ρ	17.26	17.21	17.13	17.06	

TABLE 3. COEFFICIENTS OF THERMAL EXPANSION

$10^6\ \alpha_{100}$	$-\ 22.5 \pm 1.0$
$10^6\ \alpha_{010}$	$+\ 47 \pm 2$
$10^6\ \alpha_{001}$	$+\ 94 \pm 4$

REFERENCES

[1] R. C. L. Mooney and W. H. Zachariasen, CK-1367, CK-1377, CK-1968 and CN-2069.

[2] F. J. Schnettler and E. R. Jette, LAMS-211, p. 21. F. H. Ellinger of Los Alamos Scientific Laboratory has obtained evidence that 4.624 ± 0.001 kX is a somewhat better value for the unit cell edge of delta plutonium at $350^{\circ}C$. However, there is good reason to suspect that the specific volume of the delta phase at any given temperature is strongly dependent on previous history, and it is not clear that "equilibrium" values of unit cell dimensions have ever been determined.

[3] F. J. Schnettler and E. R. Jette, LAMS-249, p. 17.

ACKNOWLEDGEMENT

The X-ray diffraction patterns upon which this investigation is based were taken by Finlay Ellinger and measured by Marian Gibbs.

The author is also indebted to Eric R. Jette, CMR Division, and to A. S. Coffinberry, Group CMR-5, for having provided the opportunity for this investigation to be carried out.